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Crystal field in $Pr_2(SO_4)_3.8H_2O$: a rigorous approach

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Abstract : An analysis of the observed magnetic susceptibility of praseodymium sulphate octahydrate in terms of the ligand field theory has been performed and the set of crystal field parameters has been evaluated. The most rigorous approach of direct diagonalization of the Hamiltonian matrix constructed in a basis of states belonging to all the atomic terms of Pr^{3+} ion has been employed. The Hamiltonian consists of terms representing free ion (consisting of Coulomb and spin-orbit) and crystal field interactions and the above procedure automatically includes J-mixing under the crystal field and the effect of the intermediate coupling scheme. It has been found that a small covalency reduction has to be introduced in order to have a good fit to the observed values. It has also been demonstrated that such rigorous calculation is necessary in order to evaluate the correct set of parameters which may widely differ from the values obtained from approximate calculations previously performed.

Keywords : Crystal field, magnetic susceptibility, J-mixing

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1. Introduction

Crystal field has an extensive influence on the diverse physical properties of the magnetic ions and a correct theory should account for all the observed optical and magnetic properties simultaneously. Hence, a precise knowledge of the crystal field (CF) parameters is considered to be important. For a correct evaluation of the crystal field parameters it is essential to adopt the most rigorous approach of direct diagonalisation of the complete matrix of the Hamiltonian that includes free ion, and crystal field interactions. The method automatically includes the effect that one obtains from intermediate coupling scheme and different J-mixing under the crystal field. Although this rigorous approach has been adopted for interpreting optical absorption data of rare earth ions by a number of workers [1–7], the magnetic data of ions (with a few exception) are often interpreted in terms of a simpler theory, not rigorous from the above point of view. The rigorous approach mentioned above, no doubt, deals with a matrix of large dimension, diagonalisation of which was a

formidable problem earlier. With the advent of fast computers having sufficient storage capacity, the problem can now be tackled with comparative ease. Of the various rare earth ions (except Ce^{3+}), Pr^{3+} and Tm^{3+} present the diagonalisation to be the easiest as they involve the matrix of smallest dimension (91 × 91) in the rare earth series. Recently, Neogy *et al* [8] have provided an analysis of magnetic data of $Pr_2(SO_4)_3.8H_2O$ and obtained CF parameters. Since no spectroscopic data is available for this sample, one has to evaluate the energy parameters from the magnetic data alone. He confined his calculation within 33 dimensional space, resulting from the states of multiplets $^3H_4$, $^3H_5$ and $^3H_6$ of the ground term ^3H or Pr^{3+}. It is to be noted that for Pr^{3+} ion, the total energy matrix spans 91 dimensional space and one has to work in 91 dimensional space for correct evaluation of CF parameters. The purpose of the present paper is to emphasize on the utility of rigorous theoretical treatment to evaluate CF parameters correctly and to interpret the thermal variation of observed magnetic susceptibility and anisotropy [9] of Pr^{3+} ion in octahydrated sulphate host. It is also intended to demonstrate to what extent the values of crystal field parameters obtained from this rigorous treatment differ from those obtained by simpler method where calculation was confined within the ground term of the Pr^{3+} ion only. If Neogy's parameters be the correct set of parameters then it would reasonably reproduce the magnetic susceptibility and anisotropy data while one works in the 91 dimensional space using these parameters. We have actually computed the values of susceptibility and anisotropy at different temperatures using Neogy's parameters in the 91 dimensional space. Results show large deviation from the experimental values. Then by extensive trial computation a new set of parameters has been evaluated to achieve reasonable agreement between theoretical and experimental susceptibility and anisotropy values. A small covalency reduction of the orbital moment improves the agreement further.

2. Theoretical consideration

2.1. Crystal field energy levels :

The effective Hamiltonian of the Pr^{3+} ion in the crystal in the absence of external field, is given by

$$H_{eff} = H_r^{ij} + H_{so} + H_{cf}, \tag{1}$$

where the H_r^{ij} is the electrostatic energy, H_{so} is the spin-orbit interaction energy and H_{cf} represents the crystal field interaction. In view of our aim to compare the theoretical results with those of the previous workers taking identical interactions, we have not considered interactions like two body configurations (α, β, γ), spin other orbit (M^0), electrostatically correlated spin-orbit (p^2) *etc.* in this work. Further, we like to stress that these interactions (represented by α, β, γ, M^0, p^2 *etc.*) produce very little effect on the magnetic susceptibility although it might have small but perceptible influence on the optical data. Following the work of Sherry [10] we assume an approximate tetragonal site symmetry for the Pr^{3+} ion in

the crystal and this makes the observed bulk magnetic data amenable to theoretical analysis without detailed knowledge of the structure. Then H_{cf} is of the form

$$H_{cf} = \sum_{i} -|e| V(i) = \sum_{i} \sum_{k,q} -|e| a_{k,q} U_q^{(k)}(i), \tag{2}$$

where $k = 2, 4, 6, q(|q| \leq k) = 0, \pm 4$, $a_{k,q}$ is the coefficient associated with the spherical harmonics Y_k^q when the crystal field potential V is expanded in terms of them and $a_{k,q} = a_{k,-q}$ for the site symmetry of the ion in our case. In (2) $U_q^{(k)} = r^k Y_k^q$ is an irreducible tensor operator and the summation over i extends over the two $4f$ electrons. Quantities like $-|e| a_{k,q} {}_{4f}\langle r^k \rangle_{4f}$ will occur in the various matrix elements of the CF interaction and they are treated as crystal field parameters denoted by B_{kq}.

The matrix of the entire Hamiltonian H_{eff} is constructed in a basis of states represented by $|SLJM_J\rangle$ considering all the states belonging to the multiplet terms ^{3}PFH ^{1}SDGI of Pr^{3+} ion and it turns out to be a 91×91 matrix. The matrix is diagonalised and a low lying group of nine levels is identified with a spread of about ~ 489 cm^{-1} which is responsible for the significant contribution to the susceptibility. The ground state comes out to be a singlet.

2.2. Covalency reduction of orbital angular momentum :

We find that unless a reduction of the orbital angular momentum matrices is assumed, presumably due to the covalency effect implying motion of the magnetic electrons in molecular orbitals, it becomes impossible to achieve a good fit to the magnetic susceptibilities. The details of the covalency reduction of the orbital angular momentum in the case of rare earth ions have been discussed elsewhere [11]. The orbital reduction is assumed to partake of the symmetry of the complex and they are represented by $k_{\parallel}$ and $k_{\perp}$.

2.3. Calculation of paramagnetic susceptibility :

As stated above, the significant contribution to the magnetic susceptibility comes from the lowest nine states resulting from the above diagonalization. We now apply Zeeman perturbation on the above nine states and the ionic paramagnetic susceptibility along and perpendicular to the symmetry axis at different temperatures has been worked out using Van Vleck's formula [12]

$$K_\alpha = N \sum \left[\frac{\left(W_\alpha^{(1)}\right)^2}{k_B T} - 2W_\alpha^{(2)} \right] \exp\left(-\frac{W^{(0)}}{k_B T}\right) \Big/ \sum \exp\left(-\frac{W^{(0)}}{k_B T}\right), \tag{3}$$

where the summation extends over all the aforesaid lowest nine states, $W^{(0)}$ is the unperturbed energy of the state in the zero magnetic field (*i.e.* crystal field energy), $W_\alpha^{(1)} H$ and $W_\alpha^{(2)} H^2$ are the first and second order energy correction of the state due to Zeeman perturbation $\beta H(k_\alpha L_\alpha + 2S_\alpha)$ when the magnetic field H is applied along the direction α. Since the lowest state is a singlet, no question of epr g-values arises from this state.

3. Results and discussion

The 91 × 91 matrix formed from the states $|SLJM_J\rangle$ of all the atomic terms of Pr^{3+} ion is diagonalised. It breaks up into four matrices of order 24, 21, 25 and 21 under a crystal field of D_{4h} symmetry. A low lying group of nine states occurs with an overall energy separation ~ 489 cm^{-1}. The ground state ψ_g is a singlet and is given by

$$\begin{aligned}\psi_g = &- 0.0023\,|{}^3P_2,2\rangle + 0.0023\,|{}^3P_2,-2\rangle + 0.0309\,|{}^3F_2,2\rangle \\ &- 0.0309\,|{}^3F_2,-2\rangle - 0.0108\,|{}^3F_3,2\rangle - 0.0108\,|{}^3F_3,-2\rangle \\ &- 0.0036\,|{}^3F_4,2\rangle + 0.0036\,|{}^3F_4,-2\rangle + 0.6977\,|{}^3H_4,2\rangle \\ &- 0.6977\,|{}^3H_4,-2\rangle - 0.0379\,|{}^3H_5,2\rangle - 0.0379\,|{}^3H_5,-2\rangle \\ &+ 0.0084\,|{}^3H_6,6\rangle - 0.0072\,|{}^3H_6,2\rangle + 0.0072\,|{}^3H_6,-2\rangle \\ &- 0.0084\,|{}^3H_6,-6\rangle + 0.0042\,|{}^1D_2,2\rangle - 0.0042\,|{}^1D_2,-2\rangle \\ &+ 0.1020\,|{}^1G_4,2\rangle - 0.1020\,|{}^1G_4,-2\rangle - 0.0013\,|{}^1I_6,6\rangle \\ &+ 0.0013\,|{}^1I_6,2\rangle - 0.0013\,|{}^1I_6,-2\rangle + 0.0013\,|{}^1I_6,-6\rangle\end{aligned}$$

It is to be noted that the ground state wavefunction quoted by Neogy *et al* [8] is incorrect, it contains the highest contribution from a state belonging to $^3H_6$ but that can never be the case. The highest contribution should come from a state belonging to the free ion ground level $^3H_4$. This is also found to be the case from the result of our diagonalization procedure. The next higher level lies ~ 2000 cm^{-1} above the ground level. So the low-lying nine states are only effective for the magnetic susceptibility calculation. The calculated energy values

Table 1. Calculated energy values alongwith the crystal quantum number μ of the ground stark level.

μ	Energy in cm^{-1}
2	0
±1	40.1
2	41.6
0	112.1
0	167.1
±1	263.9
0	489.4

of the nine stark levels (which are only used for susceptibility calculation) with highest contribution from ground multiplet $^3H_4$ alongwith the crystal quantum number μ is given in Table 1. It is to be noted that no experimental optical data are available for comparison.

After extensive trial method, we arrived at the following set of parameters which gives a good fit to the magnetic susceptibility data. E^1 = 4802.7684 cm^{-1}, E^2 = 21.6718 cm^{-1}, E^3 = 455.3607 cm^{-1}, ζ = 720.0 cm^{-1}, B_{20} = 458.4 cm^{-1}, B_{40} = −1487.67 cm^{-1}, B_{60} = −769.8 cm^{-1}, B_{44} = 303.8 cm^{-1}, B_{64} = −699.7 cm^{-1}, $k_{\parallel}$ = 0.980, $k_{\perp}$ = 0.977 where E^1, E^2, E^3 are electrostatic energy parameters which are linear combinations of Slater F^k integrals introduced by Racah [13], ζ is the spin-orbit coupling coefficient, B_{kq}'s are the crystal field parameters and $k_{\parallel}$ and $k_{\perp}$ are the anisotropic orbital reduction factors due to covalency effect. To start with, we used Neogy's set of parameters in our rigorous procedure to calculate the principal magnetic susceptibilities $K_{\parallel}$, $K_{\perp}$ and the mean susceptibility $\bar{K}$. To our surprise, the agreement between the theoretical and experimental values is found to be very poor. Throughout the temperature range from room to liquid nitrogen, this difference between the theoretical and experimental values varies from (25% to 42%), (25% to 55%) and (19% to 37%) for $\bar{K}$, $K_{\parallel}$ and $K_{\perp}$, respectively. We then systematically varied the parameters and best possible result is obtained with the set of parameters quoted above. The ranges of variation of the calculated values from experimental values for $\bar{K}$, $K_{\parallel}$ and $K_{\perp}$ are (1.5% to 26%), (2.8% to 10.7%) and (2.5% to 28%), respectively. An introduction of slight covalency reduction $k_{\parallel}$ = 0.980 and $k_{\perp}$ = 0.977 improves the agreement further and the resulting variation ranges from (0.4% to 18%), (1.0% to 7.2%) and (0.6% to 21%), for $\bar{K}$, $K_{\parallel}$ and $K_{\perp}$ respectively. The values of $k_{\parallel}$ and $k_{\perp}$ indicate that the covalency effect is very small as expected in the case of rare earth ions. The observed thermal variation of $\bar{K}$, $K_{\parallel}$ and $K_{\perp}$ are shown in Figures 1, 2 and 3 alongwith

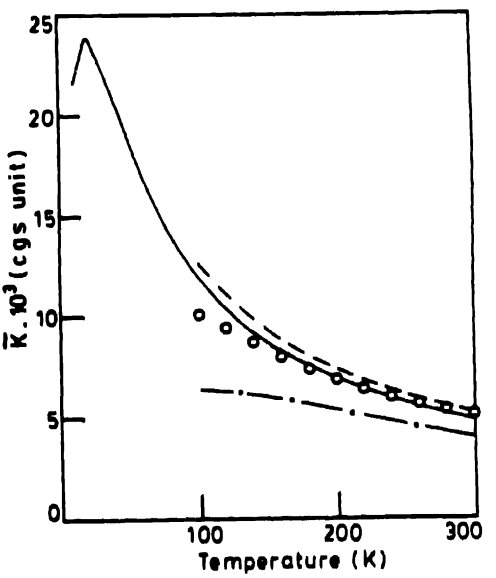

Figure 1. Thermal variation of $\bar{K}$ for Pr-sulphate octahydrate. —— theoretical curve (calculated with our parameters including covalency, - - - theoretical curve (calculated with our parameters without covalency), — · — theoretical curve (calculated with Neogy's parameters), O experimental points

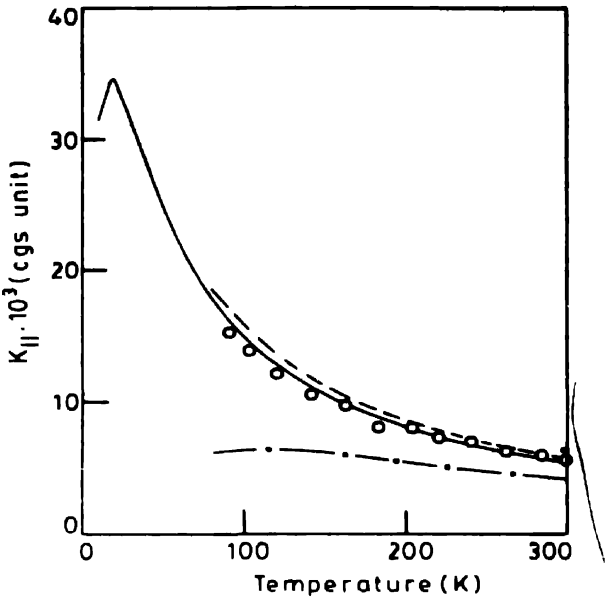

Figure 2. Thermal variation of $K_{||}$ for Pr-sulphate octahydrate. —— theoretical curve (calculated with our parameters including covalency, - - - theoretical curve (calculated with our parameters without covalency), — · — theoretical curve (calculated with Neogy's parameters), O experimental points

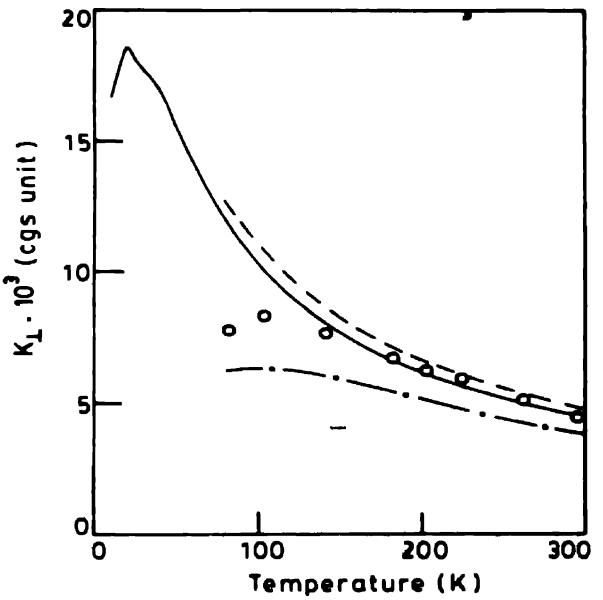

Figure 3. Thermal variation of $K_{\perp}$ for Pr-sulphate octahydrate —— theoretical curve (calculated with our parameters including covalency. - - - theoretical curve (calculated with our parameters without covalency). — · — theoretical curve (calculated with Neogy's parameters), O experimental points.

our theoretically computed curves (two sets of curves : one without covalency and the other with covalency). Each figure also includes the curve computed using Neogy's parameters for comparison. It can be noted that for $K_{\|}$, the agreement between the theory and experiment is within 7.2% at most, throughout the entire range of 80–300 K. For $\bar{K}$ and $K_{\perp}$, the agreement is within 10% from 300 K to 120 K. As the temperature is lowered from 120 K, the discrepancy between theoretical results and experimental values increases systematically. It appears that the change in the crystal field parameters with temperature, may explain the difference. Our theoretical calculations show a peak in $\bar{K}$, $K_{\|}$ and $K_{\perp}$ values at about 18–20 K contrary to Neogy's finding for ΔK and $K_{\|}$ which occurred at 40 K.

We conclude that to evaluate correct crystal field parameters, an exact diagonalisation of the complete energy matrix is necessary instead of carrying out approximate calculations as was done previously. This is obvious from the ground state quoted here, the mixing of $^1G_4$ with $^3H_4$ is much greater than that of $^3H_5$ or $^3H_6$.

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